



Preparation of the visible light responsive N³⁻-doped WO₃ photocatalyst by a thermal decomposition of ammonium paratungstate

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ABSTRACT

The nitrogen doped WO₃ (N-WO₃) photocatalyst was successfully prepared by a thermal decomposition of an ammonium paratungstate [(NH₄)₁₀W₁₂O₄₁·5H₂O] containing NH₄⁺ ions as a nitrogen source. The N-WO₃ prepared at 673–873 K efficiently absorbed visible light in longer wavelength regions as compared to a commercial N-free WO₃. Although small amount of Pt particles must be deposited on the catalyst surfaces, the N-WO₃ photocatalysts were found to decompose gaseous methanol into CO₂ and H₂O under visible or solar light irradiations. As well as, the Pt particles on the N-WO₃ surfaces to enhance the photocatalytic activity showed an oxidation catalysis property at low temperatures of 323–333 K. These results suggest that the N-WO₃ deposited with Pt particles can effectively utilize the sunlight as light and/or heat sources.

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1. Introduction

TiO₂ semiconductor has been widely studied as a photocatalysts to purify air, water and soil polluted with various hazardous chemicals [1–3]. However, TiO₂ photocatalysts necessitate UV light irradiation having wavelengths shorter than 390 nm. In our previous reports, the visible light responsive TiO₂ photocatalysts could be successfully prepared by using ion engineering techniques such as ion implantation or RF-magnetron sputtering deposition methods [4–9]. As well as, the N-doping within the TiO₂ semiconductor has recently been known to be effective for the preparation of the visible light responsive photocatalysts [10–15]. In contrast, a WO₃ semiconductor, which shows a yellow-green color, has been expected as a photocatalyst operating under visible light irradiation. However, since the photo-excited electrons in the conduction band of WO₃ semiconductor cannot reduce O₂, it has been believed that photocatalytic oxidation of organic compounds hardly occurs on such bare WO₃ surfaces. However, the WO₃ loaded with Pt or CuO cocatalysts have recently been reported to show the photocatalytic reactivity under visible light irradiation [16–18].

In this study, the N-doping within the WO₃ semiconductor was carried out in order to expand its absorption in visible light regions. As for the N-doped TiO₂ semiconductors, the visible light absorption generally appears only as a shoulder band at around 400–420 nm [10–12]. Moreover, the doping of large amounts of N³⁻ anions within the TiO₂ lattice dramatically depresses the

photocatalytic reactivity due to the formation of Ti³⁺ sites and/or oxygen vacancies as a recombination center for the photo-formed charge carriers. In contrast, the N³⁻ doping into the WO₃ lattice is expected to hardly form the recombination centers due to an efficient charge compensation effect between W⁶⁺ and N³⁻. The photocatalytic activity of the N-doped WO₃ was evaluated by the oxidation of methanol under visible or solar light irradiations as a model reaction.

2. Experimental

The N-doped WO₃ powders were prepared by thermal decomposition of ammonium paratungstate [(NH₄)₁₀W₁₂O₄₁·5H₂O], Kishida Chemical Co., Ltd.) in air condition at 473–1073 K. Small amount of Pt particle was then loaded on the N-doped WO₃ surface by a photodeposition method from H₂PtCl₆·6H₂O in aqueous methanol solution (methanol/H₂O = 50 vol%). The prepared samples were denoted as Pt(X)/N-WO₃(Y) (X: loading amount of Pt (wt%), Y: calcination temperature (K)). A commercial N-free WO₃ powder (Kishida Chemical Co., Ltd.) was used as a reference. The prepared N-WO₃ samples were then characterized by XRD (Shimadzu, XRD-6100), diffuse reflectance UV-vis absorption (Shimadzu, UV-2200A) and XPS (Shimadzu, ESCA-3200) measurements at room temperature.

The photocatalytic reactivity of the Pt/N-WO₃ samples was evaluated by decomposition of gaseous methanol under visible light or sunlight irradiations. The Pt/N-WO₃ catalysts (50 mg) were placed onto a quartz cell (volume, ca. 33 cm³). Prior to the photoreactions, the catalysts were degassed under high vacuum at 723 K for 2 h, treated in sufficient amounts of O₂ at the same temperature for

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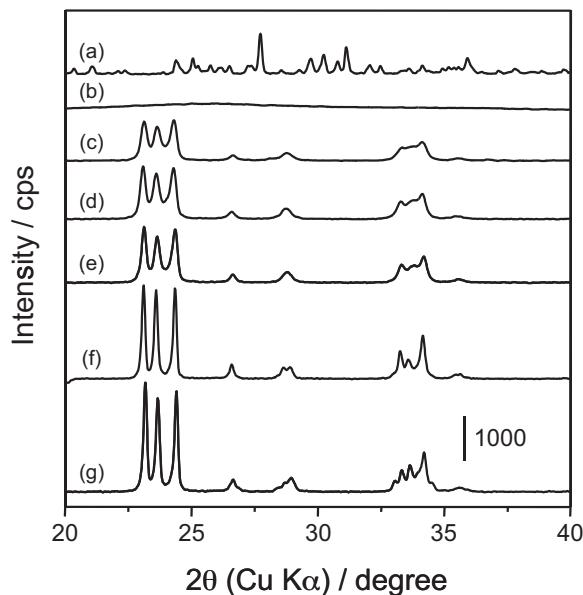


Fig. 1. XRD patterns of the N-WO₃ powders prepared by a thermal decomposition of ammonium paratungstate. (a) [(NH₄)₁₀W₁₂O₄₁·5H₂O], (b) N-WO₃(473), (c) N-WO₃(673), (d) N-WO₃(773), (e) N-WO₃(873), (f) N-WO₃(1073), and (g) commercial N-free WO₃ (reference).

2 h, and then degassed at 373 K for 2 h. A gas mixture of CH₃OH (0.27 kPa) and O₂ (0.80 kPa) was then introduced into the reaction cell. The amount of methanol introduced into the reaction cell was calculated as ca. 7 μmol. Visible light irradiation was carried out by using a 100 W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2) through a cutoff filter (Toshiba Glass, L-42 ($\lambda > 420$ nm), Y-45 ($\lambda > 450$ nm) and Y-48 ($\lambda > 480$ nm)). As for the sunlight irradiation, a commercial sunlight gathering system (Laforet Engineering, XD-50D) was used [19,20]. The sunlight collected by 12 lenses is guided by a flexible optical fiber and irradiated onto the photocatalyst in the reaction cell. As well as, this system can automatically chase the highest light intensity during sunlight irradiation. To avoid the heating effect during the sunlight irradiation, the photocatalyst in the cell was cooled in a water bath. However, the water temperature increased up to 323–333 K during the photoreaction under sunlight irradiation. The amounts of CO₂ produced in the photocatalytic reaction were then analyzed by a gas chromatography (Shimadzu, GC-14A).

3. Results and discussion

Fig. 1 shows the XRD patterns of the N-doped WO₃, commercial N-free WO₃ and ammonium paratungstate. The N-WO₃(473) did not show any peaks, showing an amorphous phase. As the calcination temperatures increased up to 673 K, three sharp peaks were observed at 23–25°, which can be assigned to the (0 0 2), (0 2 0) and (2 0 0) phases of monoclinic WO₃ crystal [21–23]. The N-WO₃(1073) showed almost same crystallinity to the commercial N-free WO₃. However, the N-WO₃ samples did not show any

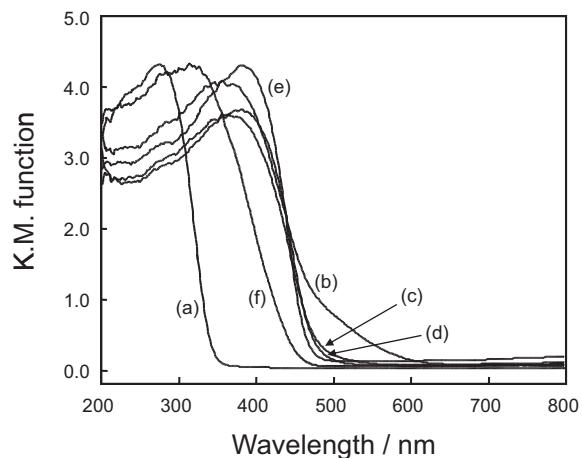


Fig. 2. Diffuse reflectance UV-vis absorption spectra of the N-WO₃ powders prepared by a thermal decomposition of ammonium paratungstate. (a) [(NH₄)₁₀W₁₂O₄₁·5H₂O], (b) N-WO₃(673), (c) N-WO₃(773), (d) N-WO₃(873), (e) N-WO₃(1073), and (f) commercial N-free WO₃ (reference).

significant peak shift in the diffraction patterns, indicating that no lattice distortion was introduced by N³⁻ doping into the WO₃ crystals. The primary particle sizes of the N-WO₃(773), N-WO₃(1073) and WO₃(commercial) were determined by Scherrer's equation as 33, 67 and 59 nm, respectively. However, SEM observations revealed very large aggregated particles of 5–8 μm (data not shown here) and the BET surface areas of these samples were quite small of 3–5 m²/g.

Fig. 2 shows the diffuse reflectance UV-vis absorption spectra of the N-doped WO₃, commercial N-free WO₃ and ammonium paratungstate. The ammonium paratungstate, which is a white powder, shows its absorption edge at around 350 nm. In contrast, as the preparation temperatures of the N-WO₃ increased from 673 to 1073 K, the sample colors changed from orange to yellow-green and their absorption edges were observed at around 500–600 nm. Although N-doped TiO₂ semiconductors are known as a visible light responsive photocatalyst, the absorption in visible light regions is generally observed as a shoulder band assigned to the formation of an impurity level due to N³⁻ anion [10–15]. However, it is notable that the absorption edges of the N-WO₃ samples smoothly shift toward visible light regions as compared to the N-free WO₃. This result indicates that the N³⁻ anion doping effectively modify the bandgap structure of WO₃ semiconductor.

In order to discuss the surface states, the W4f and O1s XPS spectra of the N-WO₃ were shown in Fig. 3. The ammonium paratungstate showed peaks at 38.9 (W4f_{5/2}) and 36.9 (W4f_{7/2}) eV. As summarized in Table 1, these peaks can be assigned to the W⁶⁺ of an insulating tungstate anion. In contrast, the N-WO₃ calcined at higher temperature than 673 K and N-free WO₃ showed typical W4f peaks at 38.0 and 35.8 eV for the stoichiometric WO₃ semiconductor surface [22,23]. However, since the N-WO₃(473) showed the W4f peaks at a little high binding energy regions of 38.6 and 36.6 eV, the amorphous WO₃ surface might have a low semiconductivity. As well as, the ammonium paratungstate and

Table 1

Assignments for the W4f XPS spectra of commercial N-free WO₃, N-WO₃ and [(NH₄)₁₀W₁₂O₄₁·5H₂O].

Samples	Binding energy (eV)		Assignments
	W4f _{5/2}	W4f _{7/2}	
N-free WO ₃ (commercial)	38.0	35.8	W ⁶⁺ on stoichiometric WO ₃ surface (semiconductivity)
N-doped WO ₃ calcined at 673–1073 K	38.0	35.8	
N-doped WO ₃ calcined at 473 K	38.6	36.6	W ⁶⁺ on amorphous WO ₃ (low semiconductivity)
Ammonium tungstate (precursor)	38.9	36.9	W ⁶⁺ in WO ₆ units of polyoxo tungstate (insulation property)

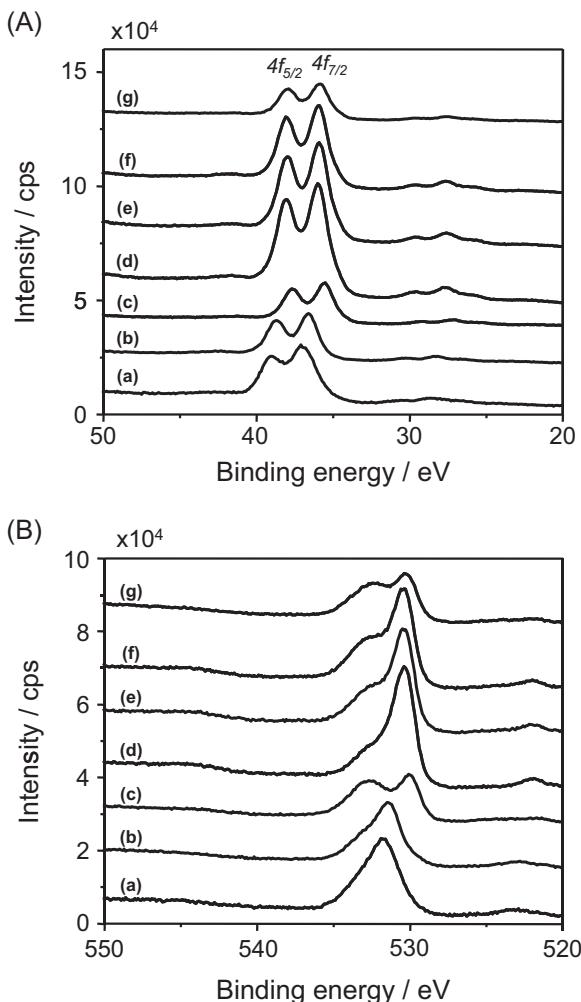


Fig. 3. W4f (A) and O1s (B) XPS spectra of (a) $[(\text{NH}_4)_10\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$, (b) N- WO_3 (473), (c) N- WO_3 (673), (d) N- WO_3 (773), (e) N- WO_3 (873), (f) N- WO_3 (1073), and (g) commercial Nfree WO_3 (reference).

N- WO_3 (473) showed a O1s peak at 531.4 eV, which can be assigned to the O^{2-} of an insulating tungstate anion or amorphous WO_3 . In contrast, the N- WO_3 calcined at higher than 673 K and commercial WO_3 samples showed typical O1s spectra at 529.7 and 532.0 eV. As summarized in Table 2, the former peak can be assigned to the lattice oxygen of WO_3 semiconductor [22–24]. The shoulder peak at 532 eV is often mentioned as surface hydroxyl groups. However, it should be correctly assigned to a shake-up satellite due to a transition from O2p anti-bonding orbital to W4f bonding orbital [25]. The shake-up satellite is generally observed for the semiconductor oxides, such as NiO , TiO_2 , Sc_2O_3 and etc., which have vacancies in the d- or f-orbitals. Since the shake-up satellite was not observed for the N- WO_3 (473) and ammonium paratungstate, these samples do not show a semiconducting character.

Table 2
Assignments for the O1s XPS spectra of commercial N-free WO_3 , N- WO_3 and $[(\text{NH}_4)_10\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$.

Samples	O1s (eV)	Assignments
N-free WO_3 (commercial)	529.7	Lattice oxygen
N-doped WO_3 calcined at 673–1073 K	531.9 (shoulder)	*Shake-up satellite
N-doped WO_3 calcined at 473 K	531.4	Amorphous WO_3
Ammonium tungstate (precursor)		WO_6 units of polyoxo tungstate

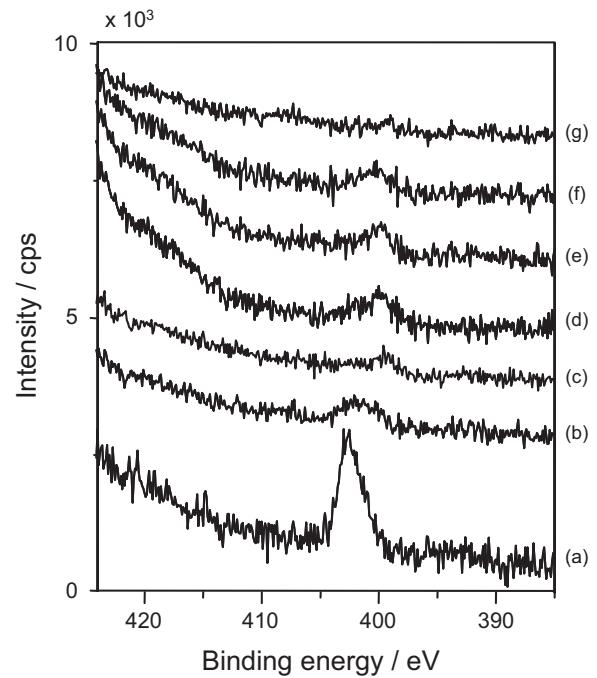


Fig. 4. N1s XPS spectra of (a) $[(\text{NH}_4)_10\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$, (b) N- WO_3 (473), (c) N- WO_3 (673), (d) N- WO_3 (773), (e) N- WO_3 (873), (f) N- WO_3 (1073), and (g) commercial Nfree WO_3 (reference).

Table 3
Assignments for the N1s XPS spectra of commercial N-free WO_3 , N- WO_3 and $[(\text{NH}_4)_10\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$.

Samples	N1s (eV)	Assignments
N-free WO_3 (commercial)	Not detected	
N-doped WO_3 calcined at ca. 400	ca. 400	N^{3-} or NO^{2-} in WO_3
N-doped WO_3 calcined at 473 K		
Ammonium tungstate (precursor)	402–403	NH_4^+ of polyoxo tungstate

For further discussion about the surface state of the N- WO_3 , the N1s XPS spectra were shown in Fig. 4 and these assignments were summarized in Table 3. The ammonium paratungstate showed a peak at 402.5 eV which can be assigned to NH_4^+ ions. The N- WO_3 samples showed a quite small peak at ca. 400 eV but the commercial N-free sample did not show any N1s peaks. Since the W-N bond in tungsten nitride is generally observed at 397.2 eV [26,27], the peak at 400 eV is supposed to be N^{3-} or NO^{2-} anions on the WO_3 surface.

The photocatalytic reactivity of the N- WO_3 was evaluated by the oxidation of methanol under visible light irradiation as a model reaction. Fig. 5(A) and (B) shows the effects of Pt loading amounts and preparation temperatures on the photocatalytic reactivity, respectively. As Abe et al. [16] have already mentioned, the N- WO_3 (873) without Pt loading did not show any photocatalytic reactivity. In contrast, the N- WO_3 (873) loaded with Pt was found to efficiently decompose methanol into CO_2 and H_2O under

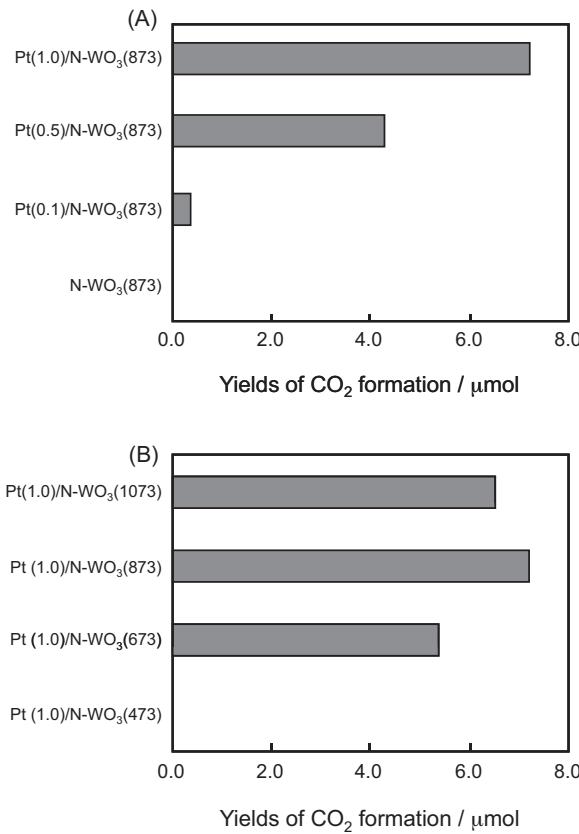


Fig. 5. Effects of Pt loading amounts (A) and preparation temperatures (B) on the photocatalytic reactivity for oxidation of methanol with O₂ on the N-WO₃ under visible light irradiation ($\lambda > 420$ nm).

visible light irradiation ($\lambda > 420$ nm). Since the initial concentration of methanol was ca. 7 μmol, the conversion to decompose methanol into CO₂ for the Pt(1.0)/N-WO₃(873) reached to almost 100%. From this result, the optimum amount of Pt to enhance the photocatalytic reactivity of the N-WO₃ was adjusted to 1.0 wt%. Moreover, as shown in Fig. 5(B), the Pt(1.0)/N-WO₃(873) showed the highest photocatalytic reactivity among the samples prepared at higher temperature than 673 K. However, the amorphous N-WO₃(473) loaded with Pt did not show any photocatalytic reactivity.

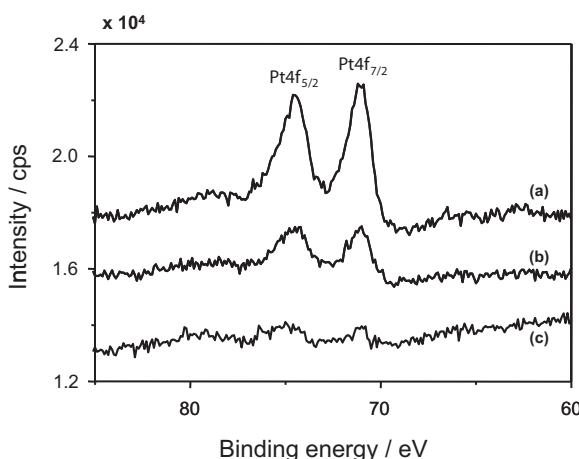


Fig. 6. Pt4f XPS spectra of the Pt-loaded N-WO₃ samples. (a) Pt(1.0)/N-WO₃(873), (b) Pt(0.5)/N-WO₃(873), and (c) Pt(0.1)/N-WO₃(873).

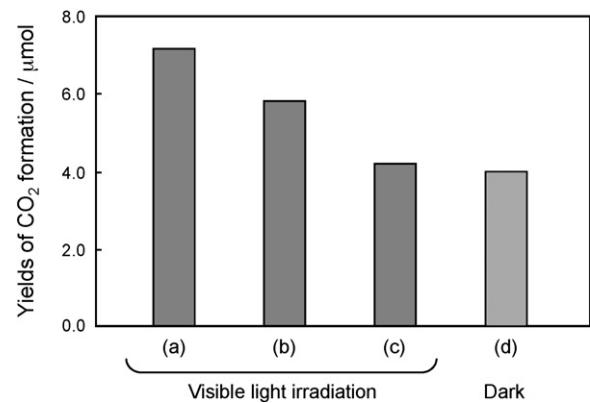


Fig. 7. Effect of the wavelengths of incident visible light on the photocatalytic reactivity of the Pt(1.0)/N-WO₃(873). (a) $\lambda > 420$ nm, (b) $\lambda > 450$ nm, (c) $\lambda > 480$ nm, and (d) under dark at 323 K.

In order to discuss the chemical state of Pt cocatalyst on the N-WO₃(873), the XPS measurements were carried out. As shown in Fig. 6, the Pt/N-WO₃(873) samples showed the photoelectron emission at 74.5 (Pt4f_{5/2}) and 71.1 (Pt4f_{7/2}) eV. Since the Pt4f_{7/2} peaks for a Pt⁰ metal and Pt²⁺ ion are generally observed at 70.9 and 73.6–74.0 eV, respectively [28–30], the Pt cocatalyst on the N-WO₃(873) is supposed to exist as a Pt⁰ metal, not as oxidized PtO or PtO₂.

Fig. 7 shows the effect of the wavelengths on the photocatalytic reactivity of the Pt(1.0)/N-WO₃(873) under visible light irradiations having different wavelengths ($\lambda > 420$, 450 and 480 nm). In fact, the commercial N-free WO₃ loaded with Pt also showed a similar photocatalytic reactivity to the Pt/N-WO₃(873) under visible light ($\lambda > 420$ nm) irradiation but did not under visible light ($\lambda > 450$ nm) irradiation (data not shown here). In contrast, the Pt(1.0)/N-WO₃(873) showed photocatalytic reactivity even under visible light irradiation having a wavelength longer than 480 nm. However, as shown in Fig. 2, the N-WO₃(873) showed a very small absorption at around 480 nm. As well as, the sample temperature was confirmed to increase up to 323–333 K during visible light irradiation. So the catalytic reactivity under dark condition at 323 K was evaluated. As a result, the Pt particle as a cocatalyst on the N-WO₃ surface also showed a catalytic reactivity to oxidize methanol into CO₂ and H₂O at 323 K. Although it is difficult to distinguish the precise distributions between photocatalytic and thermocatalytic reactivities, these results suggest that the Pt-loaded N-WO₃

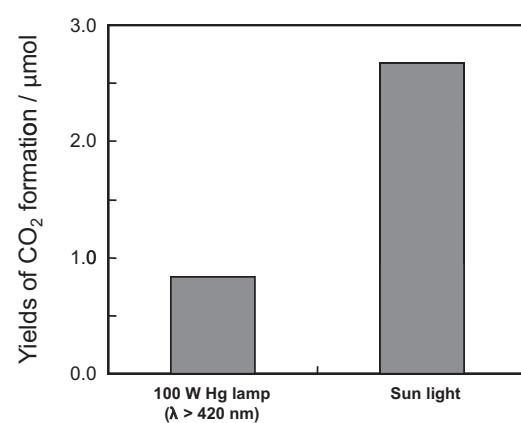


Fig. 8. Photocatalytic oxidation of methanol with O₂ on the Pt(1.0)/N-WO₃(873) under visible light from a 100 W Hg lamp or focused sunlight irradiation. Sunlight irradiation: 11:00–15:00 (4 h).

can work as a visible light responsive photocatalyst as well as a low-temperature oxidation catalyst.

Finally, the comparison of the photocatalytic reactivity of the Pt(1.0)/N-WO₃(873) under visible light from a 100 W Hg lamp or focused sunlight irradiations was shown in Fig. 8. The Pt(1.0)/N-WO₃(873) was found to completely decompose methanol of ca. 1000 ppm into CO₂ and H₂O under focused sunlight irradiation for 4 h (11:00–15:00). Since the light intensity of the focused sunlight was much higher as compared to the Hg lamp, the Pt(1.0)/N-WO₃(873) showed an efficient photocatalytic reactivity. As well as, since the temperature of the reactor increased up to 318–323 K during the focused sunlight irradiation, the Pt particles on the N-WO₃(873) surface also showed an efficient oxidation catalytic reactivity at low temperature.

4. Conclusion

A novel N^{3−}-doped WO₃ semiconductor could be prepared by a simple calcination of an ammonium paratungstate containing NH₄⁺ ions. The N-WO₃ without Pt deposition did not show any photocatalytic reactivity. However, the Pt/N-WO₃ samples showed much higher photocatalytic reactivity to decompose methanol of ca. 1000 ppm in gas phase under visible light having a wavelength longer than 450 nm or focused solar light irradiations. As well as, the Pt cocatalyst loaded on the N-WO₃ surfaces was found to work as an efficient oxidation catalyst at low temperatures of 323–333 K. These results indicate that the newly prepared N-WO₃ photocatalyst loaded with Pt cocatalyst can effectively utilize sunlight as light and/or heat sources.

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